

## DESCRIPTION

### METHOD FOR PRODUCING Ti OR Ti ALLOY THROUGH REDUCTION BY Ca

#### 5 TECHNICAL FIELD

[0001] The present invention relates to a method for producing Ti or Ti alloys through reduction by Ca, in which a metallic chloride containing titanium tetrachloride ( $\text{TiCl}_4$ ) is reduced by Ca to produce Ti metals or Ti alloys.

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#### BACKGROUND ART

[0002] A Kroll method for reducing  $\text{TiCl}_4$  by Mg is generally used as a method for industrially producing the Ti metals.  $\text{TiCl}_4$  is obtained by chlorinating titanium oxide ( $\text{TiO}_2$ ). In the Kroll method, the Ti metals are produced through a reduction step and a vacuum distillation step. In the reduction step,  $\text{TiCl}_4$  is reduced by Mg in a reactor vessel. In the vacuum distillation step, unreacted Mg and  $\text{MgCl}_2$  formed as a by-product are removed from the sponge metallic Ti produced in the reactor vessel.

[0003] In the reduction step, the reactor vessel is filled with the molten Mg, and the  $\text{TiCl}_4$  liquid is supplied from above on a liquid surface of the molten Mg. This allows  $\text{TiCl}_4$  to be reduced by Mg near the liquid surface of the molten Mg to generate the particulate metallic Ti. The generated Ti metals move sequentially downward. At the same time, the molten  $\text{MgCl}_2$  which is of the by-product is generated near the liquid surface. A specific gravity of molten  $\text{MgCl}_2$  is larger than that of the molten Mg. The molten  $\text{MgCl}_2$  which is of the by-product moves downward due to the specific-gravity difference, and the molten Mg emerges in the liquid surface instead. The molten Mg is continuously supplied to the liquid surface by the specific-gravity difference substitution, and the reducing reaction of  $\text{TiCl}_4$

proceeds continuously.

[0004] In the production of Ti metals by the Kroll method, a high-purity product is produced. However, the production cost is increased and the price of the product becomes remarkably expensive. One of factors of increased production cost is the difficulty in enhancing a feed rate of  $\text{TiCl}_4$ . The following items (a) to (c) are cited as the reason why the feed rate of  $\text{TiCl}_4$  is restricted.

[0005] (a) In order to improve productivity in the Kroll method, it is effective to enhance the feed rate of  $\text{TiCl}_4$ , i.e., to enhance a supply amount of molten Mg to the liquid surface per unit area or unit time. However, when the feed rate of  $\text{TiCl}_4$  is excessively enhanced, the rate of the specific-gravity difference substitution cannot keep up with the reaction rate, so that while  $\text{MgCl}_2$  remains in the liquid surface,  $\text{TiCl}_4$  is supplied to the  $\text{MgCl}_2$ . As a result, the supplied  $\text{TiCl}_4$  becomes lower grade chloride gases (referred to as “unreacted gas”) such as an unreacted  $\text{TiCl}_4$  gas and a  $\text{TiCl}_3$  gas, and the unreacted gas is discharged outside the reactor vessel, which reduces utilization efficiency of  $\text{TiCl}_4$ . It is necessary to avoid the generation of the unreacted gas, because a rapid increase in inner pressure of the reactor vessel is associated with the generation of the unreacted gas. Thus, there is a limit of the feed rate of  $\text{TiCl}_4$  because of the above reasons.

[0006] (b) When the feed rate of  $\text{TiCl}_4$  is enhanced, Mg vapor generated from the liquid surface of the molten Mg reacts with  $\text{TiCl}_4$  vapor to increase a precipitation amount of Ti in the inner surface of the reactor vessel above the liquid surface of the molten Mg. On the other hand, the level of the liquid surface of the molten Mg rises as the reducing reaction proceeds. Therefore, the precipitated Ti in the inner surface of the upper portion of the reactor vessel is immersed in the molten Mg at a later stage of the reducing reaction, which causes the effective area of the Mg liquid surface to be decreased to reduce the reaction rate. In order to suppress the decrease of reaction rate,

it is necessary that the feed rate of  $\text{TiCl}_4$  be restricted to prevent the Ti precipitation in the inner surface of the upper portion of the reactor vessel.

Japanese Patent Application Publication No. 8-295955 proposes a method in which the reaction efficiency is enhanced by supplying liquid  $\text{TiCl}_4$  in a dispersive manner to the liquid surface in which the molten Mg exists, and thereby the Ti precipitation is suppressed in the inner surface of the upper portion of the reactor vessel. However, the method proposed in Japanese Patent Application Publication No. 8-295955 is not enough to suppress the Ti precipitation.

[0007] (c) In the Kroll method, because the reaction is performed only near the liquid surface of the molten Mg in the reactor vessel, an exothermic area is narrowed and the temperature is locally elevated. Therefore, cooling becomes difficult, so that the feed rate of  $\text{TiCl}_4$  is restricted.

[0008] Although the feed rate of  $\text{TiCl}_4$  is not directly affected, in the Kroll method, Ti is generated in the particulate form near the liquid surface of the molten Mg, and aggregated because of wetting properties (adhesion properties) of the molten Mg, and the Ti particles is made move downward while aggregated, and then the Ti particles are sintered to grow the Ti particles by the heat generated from the molten liquid during the downward travel. Therefore, it makes difficult to recover the generated Ti by taking out Ti as fine particles to the outside of the reactor vessel, whereby the continuous production is difficult to perform and the improvement of the productivity is fettered. By reason of this, the Ti is produced in the batch process in the form of the sponge titanium.

[0009] With reference to the Ti production methods except for the Kroll method, for example, US Patent No. 2205854 describes that, in addition to Mg, for example, Ca can be used as the reducing agent of  $\text{TiCl}_4$ . US Patent No. 4820339 describes a method for producing Ti through the reducing reaction by Ca, in which the molten salt of  $\text{CaCl}_2$  is held in the reactor vessel,

the metallic Ca powder is supplied into the molten salt from above, Ca is dissolved in the molten salt, and TiCl<sub>4</sub> gas is supplied from below to react the dissolved Ca with TiCl<sub>4</sub> in the molten salt of CaCl<sub>2</sub>.

[0010] In the reduction by Ca, the Ti metals are generated from TiCl<sub>4</sub> by the reaction of the following chemical formula (1), and CaCl<sub>2</sub> as the by-product is also generated at the same time:



Ca has an affinity for Cl stronger than that of Mg, and Ca is suitable to the reducing agent of TiCl<sub>4</sub> in principle. Particularly, in the method described in US Patent No. 4820339, Ca is used while dissolved in the molten CaCl<sub>2</sub>. When the reducing reaction by Ca is utilized in the molten CaCl<sub>2</sub>, an area (reaction field) where the reaction is created is enlarged compared with the Kroll method in which TiCl<sub>4</sub> is supplied to the liquid surface of the reducing agent in the reactor vessel. Therefore, because the exothermic area is also enlarged to facilitate the cooling, the feed rate of TiCl<sub>4</sub> can be largely enhanced, and the remarkable improvement of the productivity can be also expected.

[0011] However, the method described in US Patent No. 4820339 is hardly adopted as the industrial Ti production method. In the method, because the highly expensive metallic Ca powder is used as the reducing agent, the production cost is higher than that of the Kroll method.

US Patent No. 2845386 describes another Ti production method (Olsen method) in which TiO<sub>2</sub> is directly reduced by Ca not through TiCl<sub>4</sub>. The method described in US Patent No. 2845386 is a kind of oxide direct-reduction method and is highly efficient. However, the oxide direct-reduction method is not suitable to the production of the high-purity Ti because it is necessary to use high-purity TiO<sub>2</sub>.

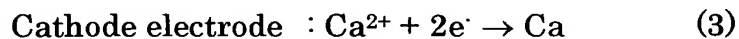
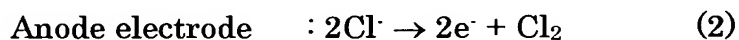
## DISCLOSURE OF THE INVENTION

[0012] It is an object of the present invention to provide a method for economically producing a high-purity Ti metals or high-purity Ti alloys with high efficiency, without using an expensive reducing agent.

[0013] In order to achieve the above object, the present inventors consider  
5 it indispensable that  $\text{TiCl}_4$  be reduced by Ca, and the present inventors look into the method for utilizing Ca dissolved in the molten salt of  $\text{CaCl}_2$  described in US Patent No. 4820339.

In the method described in US Patent No. 4820339, Ca in the molten salt is consumed in the reducing reaction reactor vessel as the  
10 reaction expressed by the chemical formula (1) proceeds, and it is necessary to continuously supply the metallic Ca powder to the reduction reactor vessel. However, in order to industrially establish the method for producing Ti through reduction by Ca, the present inventors propose a method for controlling a dissolved Ca concentration in the molten salt by electrolysis, in  
15 consideration of the fact that it is necessary that the consumed Ca of the molten salt in the reducing reaction is economically replenished.

[0014] That is, when the molten  $\text{CaCl}_2$  is electrolyzed in a reactor cell, electrode reactions expressed by the following chemical formulas (2) and (3) proceed to generate a  $\text{Cl}_2$  gas near the surface of a anode electrode while  
20 generating Ca near the surface of a cathode electrode, which allows the Ca concentration to be increased in the molten salt. Therefore, when  $\text{TiCl}_4$  is supplied to  $\text{CaCl}_2$  so as to react with Ca generated on the cathode electrode side, because Ca consumed in the Ti generation is replenished as needed, the replenishment of metallic Ca from the outside or extraction of metallic Ca  
25 becomes unnecessary, which allows the Ti metals to be economically produced.



[0015] The method for replenishing Ca, consumed in the reduction of  $\text{TiCl}_4$ ,

with Ca generated by the electrolysis can also be achieved by respectively performing the reduction and the electrolysis in a reduction cell and an electrolytic cell to circulate the molten  $\text{CaCl}_2$  between the cells. However, when  $\text{TiCl}_4$  is supplied to the molten  $\text{CaCl}_2$  in the reactor cell so as to react with Ca generated on the cathode electrode side by the electrolysis, the reactor cell can commonly be used as the reduction cell and the electrolytic cell. Therefore, because it is not necessary to separately provide the reduction cell and the electrolytic cell, there is also a great advantage from a viewpoint of installation cost compared with the case in which the molten  $\text{CaCl}_2$  is circulated between the reduction cell and the electrolytic cell.

[0016] The present invention is made based on the above conception, and the gist of the present invention pertains to a method for producing Ti or Ti alloys.

That is, a method for producing Ti or Ti alloys through reducing reaction by Ca includes: a reduction electrolysis step comprising holding a molten salt in a reactor cell to perform electrolysis in the molten salt in the reactor cell, the molten salt containing  $\text{CaCl}_2$  and having Ca dissolved in the molten salt and generating Ti or Ti alloys in the molten salt by supplying a metallic chloride containing  $\text{TiCl}_4$  to the molten salt so as to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating Ti or the Ti alloy from the molten salt in the reactor cell or outside the reactor cell.

[0017] The method of the present invention for producing Ti or Ti alloys through reduction by Ca is a method of reducing  $\text{TiCl}_4$  in which a high-purity material is easily obtained, so that the method of the present invention can produce high-purity Ti metals or high-purity Ti alloys.

Ca is used as the reducing agent to cause the metallic chloride containing  $\text{TiCl}_4$  to react with Ca in the molten salt containing  $\text{CaCl}_2$ , so that the feed rate of  $\text{TiCl}_4$  can be increased. Because the Ti particles or Ti alloy

particles are generated in  $\text{CaCl}_2$ , the aggregation of the particles and the particle growth caused by the sintering are significantly lessened, whereby it becomes possible to discharge these particles outside reactor cell, thus enabling the continuous operation to be performed. The reducing reaction and the electrolytic reaction are simultaneously caused to proceed, and Ca is replenished by the electrolytic reaction while consumed in the reducing reaction, which allows Ca to be utilized in the state in which Ca is always dissolved in the molten salt.

Accordingly, the production method of the present invention can efficiently and economically produce high-purity Ti metals or high-purity Ti alloys.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Fig. 1 is a block diagram showing a Ti metal production apparatus which exhibits an embodiment mode according to the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0019] 1. Contents of Ti or Ti Alloy Production Method according to the Invention

In the method according to the present invention for producing Ti or Ti alloys through reduction by Ca, for example, when the molten  $\text{CaCl}_2$  is held as the molten salt in a reactor cell to supply  $\text{TiCl}_4$  to the molten salt in the reactor cell,  $\text{TiCl}_4$  is reduced by Ca dissolved in the molten salt to generate Ti metals in the form of the particulate or powder (hereinafter referred to as "Ti particles"). Although the Ca dissolved in the molten salt is consumed in association with the generation of the Ti particles, Ca is generated on the cathode electrode side to replenish the consumed Ca dissolved in the molten salt because the electrolysis of the molten  $\text{CaCl}_2$  proceeds simultaneously with the reducing reaction in the reactor cell.

[0020] One of the reasons why the Ca is not conventionally used in the industrial production of the Ti metals is the difficulty in separating Ca and  $\text{CaCl}_2$ . Mg is produced by electrolyzing  $\text{MgCl}_2$ , and the generated Mg can efficiently be recovered because Mg is hardly dissolved in  $\text{MgCl}_2$ . Similarly to Mg, Na can efficiently be produced by electrolyzing NaCl. On the other hand, Ca is produced by electrolyzing  $\text{CaCl}_2$ , and it is difficult to efficiently separate only Ca because the generated Ca is dissolved in  $\text{CaCl}_2$  by about 1.5%. There is also a phenomenon in which the dissolved Ca generates  $\text{CaCl}_2$  by a back reaction (reaction in which Ca generated on the cathode electrode side is combined with  $\text{Cl}_2$  generated on the anode electrode side to return to  $\text{CaCl}_2$ ). Therefore, the production efficiency of Ca becomes worse. In this regard, although a recovery factor of Ca is improved by applying the contrivance such as cooling the electrode, the production cost of Ca inevitably remains to be still high.

[0021] In contrast, in the method of the present invention for producing Ti or Ti alloys through reduction by Ca, Ca dissolved in the molten  $\text{CaCl}_2$  is used and the separation of Ca is not necessary, so that the electrolysis production cost of Ca can be decreased.

When the reduction by Ca is utilized in the molten  $\text{CaCl}_2$ , the reducing reaction field is expanded and the heat generation/exothermic area is also enlarged. Mg has vapor pressure of 6.7 kPa (50 mmHg) at 850 °C while Ca has extremely small vapor pressure of 0.3 kPa (2 mmHg). Therefore, in the case where Ca is used for the reduction, the Ti precipitation amount becomes dramatically lessened in the inner surface of the upper portion of the reactor cell compared with Mg. Accordingly, in the method of the present invention for producing Ti or Ti alloys through reduction by Ca, the feed rate of  $\text{TiCl}_4$  can largely be increased.

In addition, Ca is inferior in wetting properties (adhesion properties) to Mg, and Ca adhering to the precipitated Ti particles is

dissolved in  $\text{CaCl}_2$ , so that the aggregation in the generated titanium particles and the particle growth caused by the sintering are significantly lessened. Therefore, the generated Ti can be taken out from the reactor cell in the form of particles, and the Ti production can continuously be operated.

5 [0022] For a supply mode of  $\text{TiCl}_4$  to the molten  $\text{CaCl}_2$  liquid, it is particularly desirable that  $\text{TiCl}_4$  be directly supplied in the gaseous state inside the molten  $\text{CaCl}_2$  liquid, because the contact efficiency of  $\text{TiCl}_4$  to Ca in the molten  $\text{CaCl}_2$  liquid is enhanced. Alternatively, it is also possible that  $\text{TiCl}_4$  is supplied in the gaseous or liquid state to the liquid surface of  
10 the molten  $\text{CaCl}_2$  liquid, or it is also possible that the liquid or gaseous  $\text{TiCl}_4$  is supplied to the liquid surface or inside the molten Ca liquid held on the molten  $\text{CaCl}_2$  liquid.

In the case where the reducing reaction is performed by supplying the  $\text{TiCl}_4$  liquid to the liquid surface of the molten Ca held on the surface of  
15 the molten  $\text{CaCl}_2$  liquid, it is desirable that the molten Ca liquid be held in a thin state to an extent in which Ca in the molten  $\text{CaCl}_2$  liquid can be utilized. When the Ca layer is thin, because Ca in the molten  $\text{CaCl}_2$  liquid is also involved in the reaction, the reaction is rendered to take place at the molten Ca layer as well as at the molten  $\text{CaCl}_2$  layer, and the Ti can continuously be  
20 generated even if the specific-gravity difference substitution cannot keep up with the reaction rate due to the increase in feed rate of  $\text{TiCl}_4$ .

[0023] With reference to the supply of the  $\text{TiCl}_4$  gas, an advantage of the method of the present invention for producing Ti or Ti alloys through reduction by Ca over the Kroll method will be described as below.

25 In the Kroll method, the  $\text{TiCl}_4$  liquid is supplied to the liquid surface of the molten Mg liquid. It is tried that the  $\text{TiCl}_4$  gas is supplied into the molten Mg liquid in order to enlarge the reaction field. However, as described above, because the Mg has the high vapor pressure, the Mg vapor intrudes in a supply nozzle of the  $\text{TiCl}_4$  gas to react with  $\text{TiCl}_4$ , which causes

a supply nozzle to be choked.

On the other hand, it is also tried that the  $\text{TiCl}_4$  gas is supplied inside the molten  $\text{MgCl}_2$  liquid. Although a choking frequency of the supply nozzle is decreased, the supply nozzle choking problem still remains. This is attributed to the fact that the melt is agitated by bubbling of the  $\text{TiCl}_4$  gas and sometimes the molten Mg reaches the supply nozzle. As much as anything, even if  $\text{TiCl}_4$  is supplied inside the molten  $\text{MgCl}_2$  liquid, the reducing reaction is difficult to occur because Mg is hardly dissolved in the molten salt.

10 [0024] On the contrary, in the method of utilizing the reduction by Ca, the nozzle choking is hardly generated and the  $\text{TiCl}_4$  gas can be supplied inside the molten  $\text{CaCl}_2$  liquid. One of the reasons why the nozzle choking is hardly generated is the small vapor pressure of the molten Ca.

That is, in the method of the present invention for producing Ti or Ti alloys through reduction by Ca, it is particularly desirable that  $\text{TiCl}_4$  be directly supplied in the gaseous state inside the molten  $\text{CaCl}_2$  liquid, and this supply mode can be applied without any problem in the actual operation. It is also possible that the liquid or gaseous  $\text{TiCl}_4$  is supplied to the liquid surface of the molten  $\text{CaCl}_2$  liquid, or it is also possible that the liquid or gaseous  $\text{TiCl}_4$  is supplied to the liquid surface or inside the molten Ca liquid held on the molten  $\text{CaCl}_2$  liquid.

20 [0025] In separating the Ti particles generated in the molten  $\text{CaCl}_2$  liquid, it is possible to separate the Ti particles from the molten  $\text{CaCl}_2$  liquid either in the reactor cell or outside the reactor cell. However, the separation becomes the batch process when the separation is performed in the reactor cell. In order to improve the productivity, the Ti particles and the molten  $\text{CaCl}_2$  liquid may be separated from each other outside the reactor cell by utilizing the Ti generated in the particulate form to discharge the Ti particles outside the reactor cell along with the molten  $\text{CaCl}_2$  liquid. The Ti particles

can simply be separated from the molten  $\text{CaCl}_2$  liquid by a squeezing operation and the like by means of mechanical compression.

[0026] In the case where Ti is produced by the method of the present invention, usually  $\text{TiCl}_4$  is used as a raw material. The Ti alloy can also be produced by using a mixture of  $\text{TiCl}_4$  and other metallic chloride. Because  $\text{TiCl}_4$  and other metallic chloride are simultaneously reduced by Ca, the Ti alloy can be produced by this method. Said other metallic chloride may be used either in the gaseous or liquid state.

[0027] In the method of the present invention for producing Ti or Ti alloys through reduction by Ca, the back reaction and the wearing of the reactor material become of issues. In the back reaction, Ca (Ca generated on the cathode electrode side or unreacted Ca) in the molten  $\text{CaCl}_2$  is combined with  $\text{Cl}_2$  generated on the anode electrode side to return to  $\text{CaCl}_2$ . The wearing of the reactor material is caused by high reactivity of Ca.

When the back reaction is generated, the electrolytic current is consumed for the back reaction, which decreases current efficiency. Particularly, for the back reaction in which Ca generated on the cathode electrode side is combined with  $\text{Cl}_2$  generated on the anode electrode side, it is desirable to separate the inside of the cell into the anode electrode side and the cathode electrode side by providing a partition wall (see Fig. 1) whose lower portion is opened.

[0028] For the problem of the wearing of the reactor material, the molten salt is formed not by single  $\text{CaCl}_2$  but by the mixed salt, and a melting point of the molten salt is decreased to effectively decrease the temperature of the molten salt (namely, bath temperature).

That is, in the method of the present invention for producing Ti or Ti alloys through reduction by Ca, basically  $\text{CaCl}_2$  having the melting point of  $780^\circ\text{C}$  is used as the molten salt. However, a binary system molten salt such as  $\text{CaCl}_2\text{-NaCl}$  and  $\text{CaCl}_2\text{-KCl}$  and a ternary system molten salt such as

CaCl<sub>2</sub>·NaCl·KCl can also be used such that at least one kind of other salts (for example, NaCl, KCl, LiCl, and CaF<sub>2</sub>) is mixed to CaCl<sub>2</sub> to form a multiple system molten salt. Therefore, because the melting point of the salt is decreased, the temperature of the molten salt (bath temperature) can be decreased. For example, when CaCl<sub>2</sub> and NaCl (having the melting point of about 800 °C) are mixed together, the melting point can be decreased to about 500 °C at the lowest.

As a result, the extension of reactor material life and the reactor material cost reduction can be achieved, and further the vaporization of Ca or the salt can be suppressed from the liquid surface.

#### [0029] 2. Embodiment mode of Ti or Ti Alloy Production Method of the Invention

An embodiment mode of the present invention will be described below with reference to the drawing.

Fig. 1 is a block diagram showing a Ti metals production apparatus according to an embodiment mode of the present invention. A reactor cell 1 in which the reducing reaction and the electrolytic reaction are concurrently generated is used in the embodiment. The reactor cell 1 holds the Ca-rich molten CaCl<sub>2</sub> in which a relatively large amount of Ca is dissolved. CaCl<sub>2</sub> has the melting point of about 780 °C, and the molten salt of CaCl<sub>2</sub> is heated to the temperature of the melting point or more.

In the reactor cell 1, the molten CaCl<sub>2</sub> which is of the molten salt is electrolyzed by passing the electric current between a anode electrode 2 and a cathode electrode 3, the Cl<sub>2</sub> gas is generated on the side of anode electrode 2, and Ca is generated on the side of cathode electrode 3. In the example, the inside of the reactor cell 1 is divided into the anode electrode side and the cathode electrode side by a partition wall 4. However, in the partition wall 4, the lower portion is opened in order that the transfer of the molten salt is not prevented.

In the reactor cell 1, the gaseous  $\text{TiCl}_4$  is injected in the dispersive manner inside the molten salt on the cathode electrode side in parallel with the electrolysis of the molten salt. Therefore, the injected  $\text{TiCl}_4$  is reduced to generate the particulate metallic Ti by the Ca dissolved in the molten salt.

5 The generated Ti particles moves downward by the specific gravity difference and accumulated at the bottom on the cathode electrode side in the reactor cell 1.

[0031] The Ti particles accumulated at the bottom of the reactor cell 1 are discharged from the reactor cell 1 along with the molten salt existing at the  
10 bottom of the reactor cell 1, and the Ti particles and the molten salt are sent to the Ti separation step (not shown). In the Ti separation step, the Ti particles discharged along with the molten salt from the reactor cell 1 are separated from the molten salt. Specifically, the Ti particles are compressed to squeeze the molten salt. The Ti particles obtained in the Ti separation  
15 step is melted to yield Ti ingots.

On the other hand, the molten salt separated from the Ti particles in the Ti separation step is the molten salt after use, in which Ca is consumed to decrease the Ca concentration. It is desirable to reuse the molten salt after use by returning it to the reactor cell. Usually, both the above  
20 separated molten salt and the molten salt after use separately discharged from the reactor cell 1 are introduced to the anode electrode side in the reactor cell 1.

[0032] Ca in the molten salt is consumed on the cathode electrode side in the reactor cell 1 as the Ti particles are generated by the reducing reaction.  
25 However, Ca is generated near the surface of the cathode electrode 3 in the cell by the electrolysis which proceeds simultaneously in the cell, and a consumed amount of Ca is replenished by the Ca generated by the electrolysis. That is,  $\text{TiCl}_4$  supplied into the molten salt is sequentially reduced in a direct manner by Ca generated near the surface of the cathode

electrode 3.

[0033] On the other hand, in the desirable mode, the molten salt after use is sent from the Ti separation step onto the anode electrode side in the reactor cell 1. Therefore, a unidirectional flow of the molten salt is formed from the anode electrode side toward the cathode electrode side in the reactor cell 1 to avoid the flow of Ca generated on the cathode electrode side into the anode electrode side. When the partition wall 4 shown in Fig. 1 is provided, the flow of Ca into the anode electrode side is effectively prevented by the combination of the partition wall 4 and the formation of the unidirectional flow. Thus, the molten salt introduced onto the anode electrode side in the reactor cell 1 is moved onto the cathode electrode side to be replenished with Ca and to become as the Ca-rich molten salt, thereby enabling to be reused for the reducing reaction.

It is desirable that the  $\text{Cl}_2$  gas generated on the anode electrode side in the reactor cell 1 be reused in a chlorination step (not shown). In the chlorination step,  $\text{TiCl}_4$  which is of the raw material of Ti is generated by the chlorination of  $\text{TiO}_2$ . The generated  $\text{TiCl}_4$  is introduced to the reactor cell 1, and  $\text{TiCl}_4$  is circularly used to generate the Ti particles by the Ca reduction.

[0034] As described above, in this embodiment mode, the generation of the Ti particles by the Ca reduction, i.e., the Ca consumption and the Ca replenishment by the electrolysis are concurrently performed in the reactor cell 1. Therefore, it is not necessary to replenish or take out Ca in the solid state, and the high-quality Ti particles are continuously and economically produced by the Ca reduction. The reactor cell 1 is commonly used as the reduction cell and the electrolytic cell, which contributes largely to an economical merit from the viewpoint of installation. The flow of Ca generated on the cathode electrode side into the anode electrode side is avoided in the reactor cell 1, so that the back reaction in which Ca reacts with the  $\text{Cl}_2$  gas generated on the anode electrode side can be prevented.

During the operation, the molten salt is managed at a temperature higher than the melting point (about 780 °C) of  $\text{CaCl}_2$  in the reactor cell 1.

#### INDUSTRIAL APPLICABILITY

5 [0035] According to the method of the present invention for producing Ti or Ti alloys through reduction by Ca, the feed rate of  $\text{TiCl}_4$  which is of the raw material can be enhanced, and the continuous production can be realized. Further, the reducing reaction and the electrolytic reaction are simultaneously caused to proceed in the reactor cell, and Ca consumed in the  
10 reducing reaction can be replenished by the electrolytic reaction, so that it is not necessary to independently handle Ca by itself.

Accordingly, the production method of the present invention can effectively be used as means for efficiently and economically producing high-purity Ti metals or high-purity Ti alloys, so that the production method  
15 of the present invention can widely be applied as the industrial method for producing Ti or Ti alloys.